Lousberg, however, proposed a rapidly interchanging conformation for the two H atoms at C(1) and C(2) based on a coupling constant $J_{\mathrm{H-H}}$ of 5 Hz measured by ^{13}C NMR experiments, by comparing this coupling constant with those of disubstituted ethanes (Lousberg *et al.*, 1970). In this aspect [2.2]metacyclophane (Emsley, Feeney & Sutcliffe, 1967) would resemble elsinochrome A more than substituted ethanes (in substituted ethanes the rotational freedom around the C—C bond is larger than in [2.2]metacyclophane); here the equatorial coupling constant of 4·0 Hz is much closer to the measured value in elsinochrome A than the 12·3 Hz for the diaxial hydrogen position.

We conclude that a fixed non-planar configuration of the elsinochrome A molecule in solution, with a diequatorial position of the H atoms at C(1) and C(2), is most likely. Comparison with compound (10) (Fig. 3) indicates that part of the high optical activity of the elsinochrome A molecule in solution may then well be due to a fixed conformational asymmetry (in addition to a contribution from the two stereocentres).

Note: Following the acceptance of this paper, the results of an X-ray structure determination were published by Meille, Malpezzi, Allegra & Nasini (1989).

References

Bear, C. A., Hall, D., Waters, J. M. & Waters, N. T. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 314–318.

Boeyens, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.

Camerman, A. & Trotter, J. (1964). *Proc. R. Soc. London Ser. A*, **279**, 129–146.

Cotrait, M., Destrade, C. & Gasparoux, H. (1975). *Acta Cryst.* **B31**, 2704–2706.

Cotrait, M. & Marsau, P. (1976). *Acta Cryst.* **B32**, 2993–2997.

Cotrait, M., Marsau, P. & Pesquer, M. (1979). *Acta Cryst.* **B35**, 2347–2351.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1358–1367.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Emsley, J. W., Feeney, J. & Sutcliffe, L. H. (1967). *High Resolution NMR Spectroscopy*, Vol. 1, pp. 168–173. Oxford: Pergamon Press.

Glusker, J. P., Carrell, H. L. & Zacharias, D. E. (1974). *Cancer Biochem. Biophys.* **1**, 43–52.

Glusker, J. P., Zacharias, D. E., Carrell, H. L., Fu, P. P. & Harvey, R. G. (1976). *Cancer Res.* **36**, 3951–3975.

Hackeng, W. H. L. (1963). Doctoral Thesis, Univ. of Utrecht, The Netherlands.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Kuroda, R. & Mason, S. F. (1981). *J. Chem. Soc. Perkin Trans.* 2, pp. 870–876.

Lapouyade, R., Koussini, R., Nourmamode, A. & Courseille, C. (1980). *J. Chem. Soc. Chem. Commun.* pp. 740–742.

Lousberg, R. J. J. Ch., Paolillo, L., Kon, H., Weiss, U. & Salemink, C. A. (1970). *J. Chem. Soc. C*, **16**, 2154–2159.

Lousberg, R. J. J. Ch., Salemink, C. A., Weiss, U. & Batterham, T. J. (1969). *J. Chem. Soc. C*, **9**, 1219–1227.

Meille, S. V., Malpezzi, L., Allegra, G. & Nasini, G. (1989). *Acta Cryst.* **C45**, 628–632.

Pontenagel, W. M. G. F. (1983). Doctoral Thesis, Univ. of Utrecht, The Netherlands.

Spek, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA; implemented and extended by the Dutch X-ray System Group.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Stezowski, J. J. (1976). *J. Am. Chem. Soc.* **98**, 6012–6018.

Acta Cryst. (1990). C**46**, 271–273

Zwitterions in Crystalline Aminophosphonic Acids. I.* Structure of (2-Pyridylmethyl)phosphonic Acid

By Zdzisław Gałdecki and Wojciech M. Wolf

Institute of General Chemistry, Technical University of Łódź, Żwirki 36, 90–924 Łódź, Poland

(*Received* 19 *January* 1989; *accepted* 24 *April* 1989)

Abstract. $C_6H_8NO_3P$, $M_r = 173·11$, monoclinic, $P2_1/c$, $a = 7·855\,(3)$, $b = 10·857\,(4)$, $c = 8·714\,(3)$ Å, $\beta = 106·18\,(3)°$, $U = 713·7\,(5)$ Å^3, $Z = 4$, $D_m = 1·60$ (by flotation in aqueous KI solution), $D_x = 1·61$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·54178$ Å, $\mu = 29·28$ cm^{-1}, $F(000) = 360$, room temperature, $R = 0·048$ for 935 observed reflections $[F > 3\sigma(F)]$. Hydrogen bonds link the molecules in a three-dimensional network. The negative charge is delocalized on the $\mathrm{O}\cdots\overset{\ominus}{\mathrm{P}}\cdots\mathrm{O}$ system, while the positive charge is spread over the pyridyl moiety.

Introduction. Organophosphorus derivatives of pyridine and quinoline with the phosphonic group *ortho*

---

[*] Part II: Gałdecki (1990).

or *para* with respect to the heterocyclic N atom are reported to be effective bactericides and herbicides (Kostka & Ochocki, 1987, and references therein). Phosphonic acid analogues of these substrates can inhibit the activity of enzymes involved in the metabolism of amino acids (Sawka-Dobrowolska & Kowalik, 1988, and references therein). Aminophosphonic acid molecules usually exist as zwitterions: the amino groups are protonated while the phosphonic acid groups are ionized. They are powerful ligands towards numerous transition-metal ions, and form stable complexes with technetium [for complexes with long-life technetium isotopes, see Faggiani, Lock, Epps, Kramer & Brune (1988, and references therein)]. In this and related papers we report X-ray structure analyses of a series of aminophosphonic acids, including (2-quinolylmethyl)phosphonic acid (Gałdecki, 1990), (4-pyridylmethyl)phosphonic acid (Wolf & Gałdecki, 1990), and their complexes with technetium and selected transition-metal ions.

Experimental. (2-Pyridylmethyl)phosphonic acid was synthesized by Kostka & Ochocki (1983). Colourless crystals were grown by slow evaporation from water. Four specimens were cut from the best-looking prisms, shaped to approximate isometrical dimensions and examined using oscillation and Weissenberg photographs. Crystal dimensions 0·5 × 0·45 × 0·5 mm; Syntex $P2_1$ automated diffractometer, graphite-monochromated Cu $K\alpha$ radiation; accurate cell dimensions by least-squares calculations from the angular settings of 15 reflections ($17 < \theta < 30°$); $\theta/2\theta$ scan mode; no significant intensity variations of three standard reflections, $2\theta_{\max} = 115°$; $h\ -8\rightarrow 8$, $k\ -1\rightarrow 11$, $l\ -1\rightarrow 9$; $R_{\rm int} = 0{\cdot}021$; 959 unique reflections; no absorption correction; 935 reflections with $F > 3\sigma(F)$ were considered observed and used in further calculations. Structure solved by direct methods; refinement on F by standard full-matrix least squares and difference electron density syntheses; all H atoms located on difference Fourier maps calculated after two cycles of anisotropic refinement. H2 refined using a riding model on its parent O2 atom with a fixed isotropic temperature factor of 0·12 Å^2; all other H atoms included in the refinement without restrictions; unit weights; final $R = 0{\cdot}048$, $S = 1{\cdot}10$; max. $(\Delta/\sigma) = 0{\cdot}075$ for the y coordinate of H1. The highest peak in the final ΔF map was 0·26, largest minimum $-0{\cdot}49$ e Å^{-3}; scattering factors as in *SHELX76* (Sheldrick, 1976); all calculations performed using programs incorporated in the *CRYSRULER* package (Rizzoli, Sangermano, Calestani & Andreetti, 1986), *i.e.* *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *SHELX76* (Sheldrick, 1976), *PARST* (Nardelli, 1983) and *ORTEPII* (Johnson, 1976). All calculations were carried out on an Amstrad PC 1512 microcomputer.

Discussion. A view of the molecule with the atom labelling is given in Fig. 1. The final atomic coordinates are summarized in Table 1,* bond lengths and valency angles are in Table 2.

The molecule of the title compound exists as a zwitterion (Fig. 2). Negative charge is spread over the O1—P—O3 fragment of the phosphonic group. The P—O1 and P—O3 bonds are equal within experimental error [1·507 (3) and 1·500 (2) Å respectively]. This suggests that the electron density is equally distributed between both O atoms. The P—O2 bond is longer [1·572 (3) Å], and the O2 atom is bound to an H atom; this indicates that P—O2 is essentially a single bond. The P—C1 bond length [1·826 (5) Å] is similar to those found in the β form of aminomethylphosphonic acid [1·817 (3) Å] (Darriet, Darriet, Cassaigne & Neuzil, 1975). Longer bonds were observed in 1-(1-phenylethylamino)benzylphosphonic acid sesquihydrate, 1·853 (3) Å (Sawka-Dobrowolska & Kowalik, 1988); α-(isopropylamino)salicylphosphonic acid hemihydrate, 1·858 (3) Å (Sawka-Dobrowolska, 1985); and (*S*)-2-methyl-1-[(*R*)-1-phenylethylamino]-1-propanephosphonic acid monohydrate, 1·856 (5) Å (Sawka-Dobrowolska, Głowiak, Kowalik & Mastalerz, 1985).

Valency angles within the phosphorus coordination sphere range from 104·6 (2) to 116·3 (2)°, the largest being the O1—P—O3 angle and the smallest being the O2—P—C1 angle. This suggests a substantially repulsive Coulombic interaction between the two O atoms bearing the negative charge.

The N atom of the pyridyl ring is protonated and is in an essentially planar configuration, the sum of

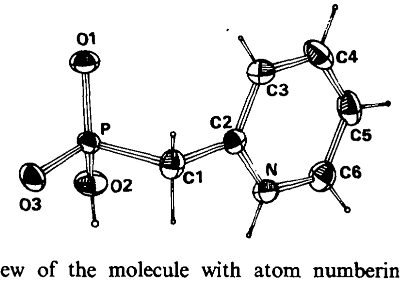

Fig. 1. View of the molecule with atom numbering. Thermal ellipsoids are drawn at the 50% probability level.

---

* Lists of structure factors, anisotropic thermal parameters, bond distances involving H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52168 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors of non-*H *atoms with e.s.d.'s in parentheses*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}(Å^2)
P	0·2812 (1)	0·0945 (1)	0·5345 (1)	0·0207 (3)
O1	0·3354 (4)	−0·0334 (3)	0·5963 (4)	0·029 (1)
O2	0·4385 (4)	0·1640 (3)	0·4934 (4)	0·030 (1)
O3	0·2046 (4)	0·1752 (3)	0·6383 (4)	0·031 (1)
N	0·2241 (5)	0·0845 (3)	0·1125 (4)	0·022 (1)
C1	0·1106 (6)	0·0820 (4)	0·3438 (5)	0·026 (1)
C2	0·1703 (5)	0·0165 (4)	0·2174 (5)	0·020 (1)
C3	0·1759 (6)	−0·1098 (4)	0·2059 (6)	0·029 (1)
C4	0·2357 (6)	−0·1638 (5)	0·0865 (6)	0·033 (1)
C5	0·2872 (6)	−0·0900 (5)	−0·0220 (6)	0·033 (1)
C6	0·2804 (6)	0·0351 (4)	−0·0068 (6)	0·029 (1)

Table 2. *Bond lengths* (Å), *valency angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

P—O1	1·507 (3)	C1—C2	1·492 (7)
P—O2	1·572 (4)	C2—C3	1·376 (6)
P—O3	1·500 (4)	C3—C4	1·385 (8)
P—C1	1·826 (4)	C4—C5	1·383 (8)
N—C2	1·332 (6)	C5—C6	1·367 (7)
N—C6	1·349 (7)		
O1—P—O2	111·2 (2)	N—C2—C1	117·9 (4)
O1—P—O3	116·3 (2)	N—C2—C3	118·7 (4)
O1—P—C1	108·6 (2)	C1—C2—C3	123·5 (4)
O2—P—O3	109·3 (2)	C2—C3—C4	120·0 (4)
O2—P—C1	104·6 (2)	C3—C4—C5	119·6 (5)
O3—P—C1	106·0 (2)	C4—C5—C6	118·9 (5)
C2—N—C6	122·9 (4)	N—C6—C5	120·0 (4)
P—C1—C2	113·9 (3)		
O1—P—C1—C2	−61·0 (4)	P—C1—C2—C3	81·5 (5)
O2—P—C1—C2	57·9 (4)	P—C1—C2—N	−97·2 (4)
O3—P—C1—C2	173·3 (3)		

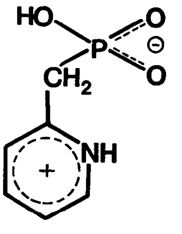

Fig. 2. Schematic representation of negative and positive charges in a molecule of the title compound.

valency angles around this atom being 360°. The pyridyl ring is almost flat; deviations from the least-squares mean plane are N −0·008, C2 −0·05, C3 −0·003, C4 0·007, C5 −0·004, C6 −0·003 Å. The n_π orbital of the N atom is perpendicular to the plane of the ring, and, following Hückel's rule, is conjugated with π orbitals of the other ring atoms. Therefore it might be expected that the positive charge formally localized on the N atom is spread over the whole pyridyl ring.

The conformation of the non-H skeleton of the molecule is described by the torsion angles summarized in Table 2.

In a similar fashion to previously reported aminophosphonic acids, molecules of the title compound are bound together by a system of intermolecular hydrogen bonds. The main interactions are those between N and O3′(x, $\frac{1}{2}-y$, $\frac{1}{2}-z$) atoms. The interatomic distances N···O3′, N—H1 and H1···O3′ are 2·627 (5), 0·95 (6) and 1·67 (6) Å respectively. There is also one short intermolecular contact [2·559 (5) Å] between O1 and O2″($1-x$, $-y$, $1-z$), which may indicate hydrogen bonding. However, the position of the H2 atom bonded to O2, as determined unambiguously from several ΔF maps, is such that the O2″—H2″···O1 angle is 51°. This is quite opposite to the commonly accepted geometrical properties of hydrogen-bond systems (Olovsson & Jönsson, 1976), and we therefore suppose that H2 is not involved in hydrogen bonding. A similar situation has been reported for 1-(1-phenylethylamino)benzylphosphonic acid sesquihydrate (Sawka-Dobrowolska & Kowalik, 1988) in which one H atom of the water molecule does not participate in the hydrogen-bond system.

The authors wish to thank Dr Justyn Ochocki for the gift of crystals. The work received support from project RP.II.10 of the Polish Ministry of National Education.

References

Darriet, M., Darriet, J., Cassaigne, A. & Neuzil, E. (1975). *Acta Cryst.* **B31**, 469–471.

Faggiani, R., Lock, C. J. L., Epps, L. A., Kramer, A. V. & Brune, D. (1988). *Acta Cryst.* **C44**, 777–779.

Gałdecki, Z. (1990). *Acta Cryst.* **C46**. Submitted.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kostka, K. & Ochocki, J. (1983). *Chem. Anal.* (*Warsaw*), **28**, 717–726.

Kostka, K. & Ochocki, J. (1987). *Pol. J. Chem.* **61**, 177–188.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L. Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Olovsson, J. & Jönsson, P.-G. (1976). *The Hydrogen Bond, Recent Developments in Theory and Experiments,* edited by P. Schuster, G. Zundel & C. Sandorfy, pp. 393–457. Amsterdam: North-Holland.

Rizzoli, C., Sangermano, V., Calestani, G. & Andreetti, G. (1986). *CRYSRULER* package, version. 1.1. Univ. of Parma, Italy.

Sawka-Dobrowolska, W. (1985). *Acta Cryst.* **C41**, 84–86.

Sawka-Dobrowolska, W., Głowiak, T., Kowalik, J. & Mastalerz, P. (1985). *Acta Cryst.* **C41**, 1773–1776.

Sawka-Dobrowolska, W. & Kowalik, J. (1988). *Acta Cryst.* **C44**, 1624–1627.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Wolf, W. M. & Gałdecki, Z. (1990). In preparation.